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# Modeling of a Buss-Kneader as a Polymerization Reactor for Acrylates. Part II: Methyl Methacrylate Based Resins

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The Buss-Kneader has proven to be a suitable reactor for the polymerization of acrylates. In this second part, the polymerization of methyl methacrylate and the ter-polymerization of methyl methacrylate (MMA), hydroxyethyl methacrylate and n-butylmethacrylate is carried out in a pilot Buss-Kneader. The reactor had to be pressurized up to about 10 bars to avoid evaporation of MMA. Instabilities in output rate and temperature profiles were observed as a result of fluctuating die pressures. Because of good mixing there may be no diffusion limitation for radicals. As a result, even at high conversions, no gel effect was observed.

## INTRODUCTION

Part I of this paper proved that the Buss-Kneader is a suitable polymerization reactor for several acrylates for the production of acrylic resins. Methyl methacrylate (MMA) is one of the main components of acrylic resins used in the coating industry. The polymerization of MMA has been carried out successfully in twin-screw extruders (1, 2). Until now, no study of the polymerization of MMA in a Buss-Kneader has been published.

The polymerization of methyl methacrylate differs in three ways from the co-polymerization of nBA and HEMA:

- DSC experiments with MMA (3) show the occurrence of a gel effect (4) by a strong increase of the polymerization at conversions above 50%.
- The produced polymer is highly viscous (1). This can result in considerable viscous dissipation of energy during a reactive extrusion process.
- Owing to the high vapor pressure of MMA, a pressure of several bars within the extruder is required to avoid evaporation at the reaction

temperature between 100°C and 160°C. At these temperatures, the vapor pressure is in the range of 1 to 4 bar.

To study these aspects, the homo-polymerization of MMA is carried out within a pilot Buss-Kneader. Finally, ter-polymer acrylic resins, based on MMA, n-butylacrylate (nBA) and hydroxyethyl methacrylate (HEMA) are prepared. Such ter-polymers are applied in coating industry.

## REACTOR MODEL

In part I of this paper, the axial dispersion model was applied successfully to describe the co-polymerization of nBA and HEMA. Axial temperature profiles, conversion and molecular weights could be calculated, although the polymerization kinetics had to be adjusted compared to the kinetics measured by DSC. A decreased polymerization rate had to be used in the reactor model.

The reactor model developed (part I) is used to discuss the experimental results on the homo-polymerization of methyl methacrylate and the production of the ter-polymer acrylic resin.

## EXPERIMENTAL SETUP

The polymerization reactions are carried out in a pilot Buss-Kneader PR 46 ( $D = 46$  mm,  $L/D = 15$ ,  $V = 0.5$  l)

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equipped with kneading elements over its entire length. For ter-polymerization, the different monomer types are premixed. Peroxide and monomers are dosed separately through an inline static mixer. The static mixer provides a micro-mixed feed of monomers and peroxide. The flow rate is varied between 1 and 6.6 l/h and the screw rotation speed between 60 and 285 rpm. Temperature settings of screw and barrel were 125°C in all cases. Different dies were used to discharge the product. Contrary to the experiments described in part I, the kneader was completely filled during all experiments. In the experiments with MMA, a fully filled kneader was ensured by increasing the flow rate at a constant screw speed until a pressure at the inlet of 5–10 bars was reached. This pressure is above the vapor pressure of MMA at the reaction temperature of max. 150°C. In the ter-polymerization of MMA, HEMA, and nBA, it was possible to adjust the die resistance to obtain an inlet pressure of 5–10 bars to ensure a fully filled kneader.

The monomer contents of the output are analyzed by gas chromatography. The molecular weight is measured with a GPC apparatus equipped with two mixed C 5  $\mu$ m columns in series calibrated with pMMA narrow standards.

### HOMO-POLYMERIZATION OF METHYL METHACRYLATE

The free radical addition homo-polymerization of MMA (BASF) was carried out in the pilot Buss-Kneader. The reaction was initiated by the peroxide tert-butyl peroxy-2-ethylhexanoate. A 50% solution of this peroxide in iso-dodecane, was used (Luperox 26R-M-50, Elf Atochem). The initiator flow rate was adjusted to obtain a 0.5 mol% concentration of active peroxide within the reaction mixture.

#### Polymerization Kinetics

The kinetic scheme for a radical addition polymerization is given in Table 1. Fleury (3) studied the polymerization kinetics of the bulk-polymerization of MMA by differential scanning calorimetry (DSC). These DSC experiments show an increase of the polymerization rate at conversions above 50%. This phenomenon is known as the gel effect or Trommsdorff effect (4). At these high conversions, there is a strong increase of the viscosity. As a consequence, the diffusion of the polymer radicals decreases and therefore the termination rate decreases. Fleury (3) described the observed gel effect for the polymerization of MMA based on an empirical diffusion model developed by Chiu *et al.* (5). In this model the termination rate constant  $k_t (= k_{t,c} + k_{t,d})$  reads:

$$k_t = k_{t,0} \cdot \frac{1}{1 + \frac{\gamma \cdot k_{t,0}}{e^{(\alpha - \beta \cdot X)}}} \quad (1)$$

with:

$$\alpha = \alpha_0 + Ln(C_{t0}/C_{t0, min})^{0.56} \quad (2)$$

**Table 1. Kinetic Scheme for the Free Radical Addition Polymerization.**

Decomposition of peroxide	$I \xrightarrow{k_d} xR^\cdot$
Initiation of monomers	$R^\cdot + M \xrightarrow{k_i} P_1^\cdot$
Propagation	$P_n^\cdot + M \xrightarrow{k_p} P_{n+1}^\cdot$
Termination (combination)	$P_n^\cdot + P_m^\cdot \xrightarrow{k_{t,c}} D_{n+m}$
(disproportionation)	$P_n^\cdot + P_m^\cdot \xrightarrow{k_{t,d}} D_n + D_m$

where  $k_x$  are the corresponding rate constants and depend on temperature according to the Arrhenius correlation:

$$k = A_0 \cdot e^{-\frac{E_A}{R \cdot T}}$$

$P_n$  denotes a growing copolymer (radical) of  $n$  monomer units.  $D_n$  denotes a dead copolymer of  $n$  monomer units.  $x$  stands for the number of radicals produced from decomposition of 1 peroxide molecule.

$$\beta = \beta_0 + \frac{T - T_{gP}}{T_{ref} - T_{gP}} + 2.32 \cdot \left[ 1 - e^{-\left(\frac{C_{t0}/C_{t0, min}}{3.34}\right)} \right] \quad (3)$$

$$\gamma = 1 \quad (4)$$

This empirical model will also be used in this paper to describe the possible occurrence of the gel effect during the polymerization of MMA. All kinetic constants, except the peroxide efficiency, are obtained from literature and presented in Table 2. The exact value of the peroxide efficiency is not known. The kinetic constants are based on measurements using benzoyl peroxide as initiator, assuming a peroxide efficiency of 1 (6). However, according to the literature, the peroxide efficiency is decreasing at increasing conversions (7). Besides that, the kinetics depend on the type of peroxide used.

#### Pressure Control and Process Stability

For twin-screw extrusion, high die-pressures can be applied to maintain the vapor pressure. Stuber *et al.* (1) reported die pressures of about 100 bars, and pressure gradients are relatively steep. In a Buss-Kneader, steep pressure gradients cannot be obtained as a result of the interrupted flights, especially when kneading elements are used (8). Kneading elements were used during the experiments for their good self-cleaning properties. If a pressure gradient exists, negative or positive, the Kneader is completely filled. In this case the die pressure has a relatively large influence on the degree of fill (Fig. 1). Therefore the Kneader will empty itself rapidly when the die pressure drops

Table 2. Kinetic Parameters Polymerization of MMA.

Kinetic constant	Value	Unit	Reference
$k_d$ (Luperox 26R-M-50)	$3.83 \cdot 10^{14} \cdot e^{-\frac{129652}{R \cdot T}}$	$s^{-1}$	Elf Atochem
$x$ (Luperox 26R-M-50)	2	—	
$k_{t,0}$	$98000 \cdot e^{-\frac{3000}{R \cdot T}}$	$m^3 mol^{-1} s^{-1}$	(6)
$k_{t,c}/k_{t,d}$	$\sim 0$ ( $T > 70^\circ C$ )	—	(6)
$k_p$	$492 \cdot e^{-\frac{18220}{R \cdot T}}$	$m^3 mol^{-1} s^{-1}$	(6)
$f_i$	0 – 1	—	adjusted
$\alpha_0$	14.14	—	(3)*
$\beta_0$	14.34	—	(3)*
$C_{10,min}$	2	$mol m^{-3}$	(3)*
$T_{gp}$	114	$^\circ C$	(3)*
$T_{ref}$	123.3	$^\circ C$	(3)*
$\Delta H_p$	56000	$J mol^{-1}$	(3)

\*Validated for  $135 < T < 165^\circ C$  and  $2 < C_{10} < 200 mol/m^3$

slightly. This mechanism can give rise to instabilities during reactive extrusion (9). The die pressure strongly depends on viscosity. In reactive extrusion, the viscosity depends exponentially on conversion. The coupling of both phenomena induces large changes in die pressures and therefore in the degree of fill. Van der Goot reported such instabilities during the co-polymerization of styrene and butyl methacrylate in a counter-rotating twin-screw extruder (10, 11). Jongbloed reported instabilities for the co-polymerization of butyl methacrylate and hydroxyethyl methacrylate (12).

Comparable instabilities were obtained when a die plate was used during the polymerization of MMA within a pilot Buss-Kneader. The discharge opening of the die has a diameter of 15 mm and an axial length of about 2 mm. The die pressure was adjusted by covering the die opening partly. Instabilities arose at

throughputs above 3 l/h and appeared as fluctuations in output rate, in- and outlet pressure and in temperatures of the reaction mixture measured at several axial positions. Because of the short axial length of the die-plate, a local change of the viscosity results in an immediate change of the die pressure. In order to prevent these instabilities, the experimental setup was modified. A heated die tube with an internal diameter of 15 mm and an axial length of 10 cm was used this time. Local changes in viscosity within the die tube are averaged and the die pressure is less dependent on viscosity changes. A stable process could be obtained in this case up to flow rates of 6.6 l/h.

Using a gear pump as discharge unit will make the output rate independent of the viscosity of the extruded material, resulting in stable processing. This, however, has not been studied during this work.

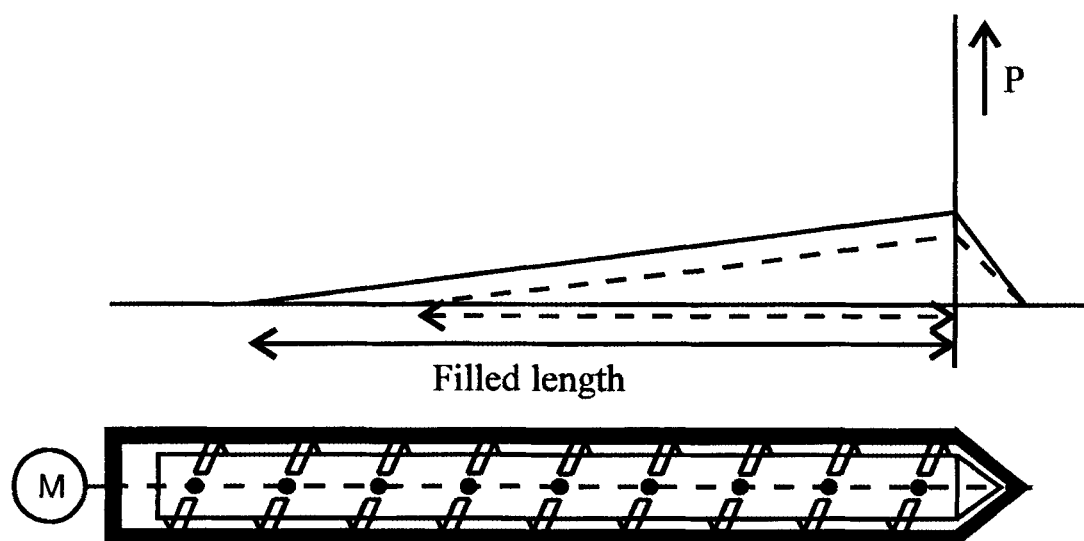


Fig. 1. Influence of die pressure on degree of fill within an extruder or Buss-Kneader. A small change of the die pressure results in a large change of the degree of fill.

## Results

The measured mass output rate was generally slightly lower than the volumetrically measured input rate, especially at low conversions of the product. This is due to evaporation of MMA at the die. Conversions were calculated as the product of the ratio of the input rate over the output rate and the polymer content of the sample:

$$X = \frac{\text{mass input rate}}{\text{mass output rate}} \cdot (1 - M) \quad (5)$$

where  $M$  is the monomer content within the sample.

Similar to the findings in part I, calculations based on the polymerization kinetics including the gel effect appear to deviate strongly from experimental results. The dotted curves in Fig. 2 and Fig. 3 show that both the temperature increase and the conversion as calculated are much larger than those obtained by experiments. However, when calculations are performed neglecting the gel effect, much better agreement between model and experiment is obtained (solid curves, Figs. 3 and 4). This leads to the contention that possibly no gel effect occurs when this radical polymerization is carried out in high-intensity mixing devices. The gel effect is related to a decrease of the mobility of the growing chains. This results in a decreasing termination velocity, leading to an increased reaction velocity and an increased molecular weight. Over the last decade, some studies were performed to understand

the occurrence of the gel effect quantitatively (13). Shear stress within extruders might increase the mobility of the polymer chains as a result of molecular orientation and destruction of entanglements. As discussed previously, the peroxide efficiency is not known exactly. Decreasing the peroxide efficiency results in further improved correspondence between calculated and measured conversions (Fig. 3).

Higher temperatures were obtained at increasing screw speeds as a result of viscous dissipation.

In all cases the obtained polymer had a number average molecular weight of about 20 kg/mole and a weight average molecular weight of about 120 kg/mole.

## PREPARATION OF AN ACRYLIC RESIN FOR COATING PURPOSES

Ter-polymers of MMA, nBA and HEMA (BASF) were produced at three fixed compositions: MMA:nBA:HEMA = 70:15:15 wt%, MMA:nBA:HEMA = 35:30:35 wt% and MMA:nBA:HEMA = 45:20:35 wt%. When acrylic resins are prepared for powder-coating purposes, the molecular weight of the polymer has to be relatively low and therefore a high peroxide concentration is required. The flow rate of the peroxide was adjusted to obtain a peroxide concentration in the reaction mixture of 2.4 wt% tert-amyl peroxy-2-ethylhexanoate (Luperox 575, Elf Atochem). In addition 0.6 wt% of the relatively slow decomposing tert-butyl

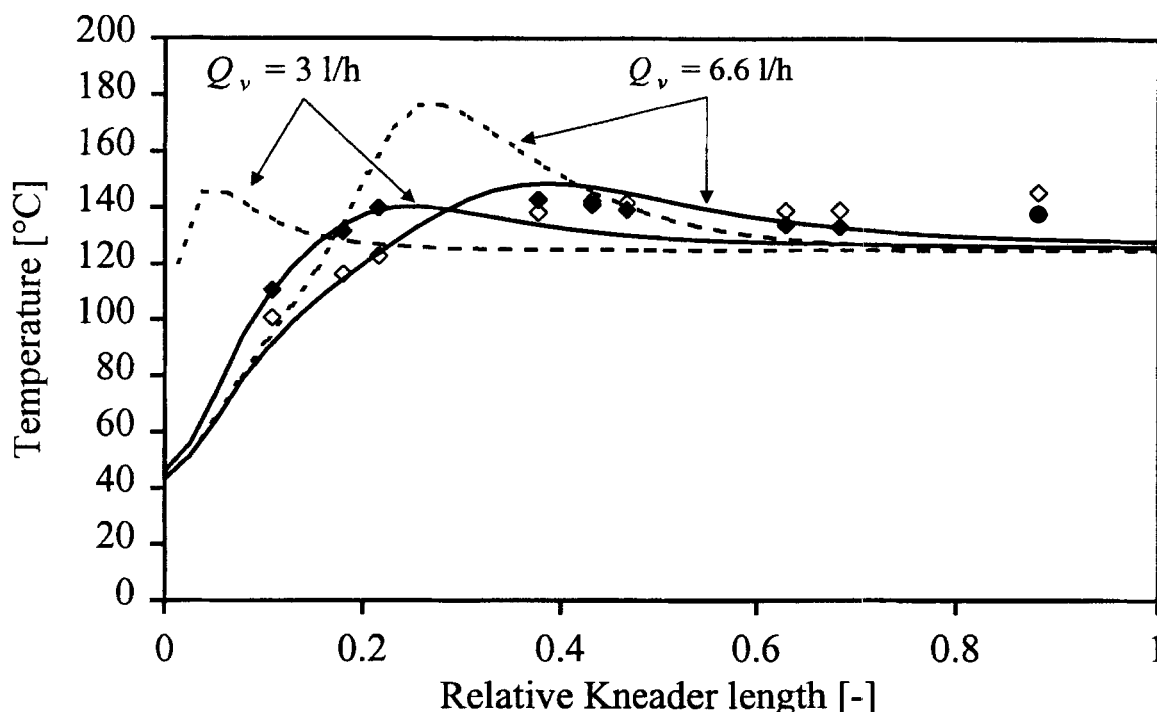


Fig. 2. Polymerization of MMA within Buss-Kneader. Measured and calculated axial temperature profiles. Temperature settings of screw and barrel: 125°C, peroxide efficiency  $f_i = 1$ .  $Q_v = 3$  l/h,  $N = 100$  rpm ( $\blacklozenge$ );  $Q_v = 6.6$  l/h,  $N = 220$  rpm ( $\diamond$ ); Calculated, gel effect neglected (—); Calculated, including gel effect (---).

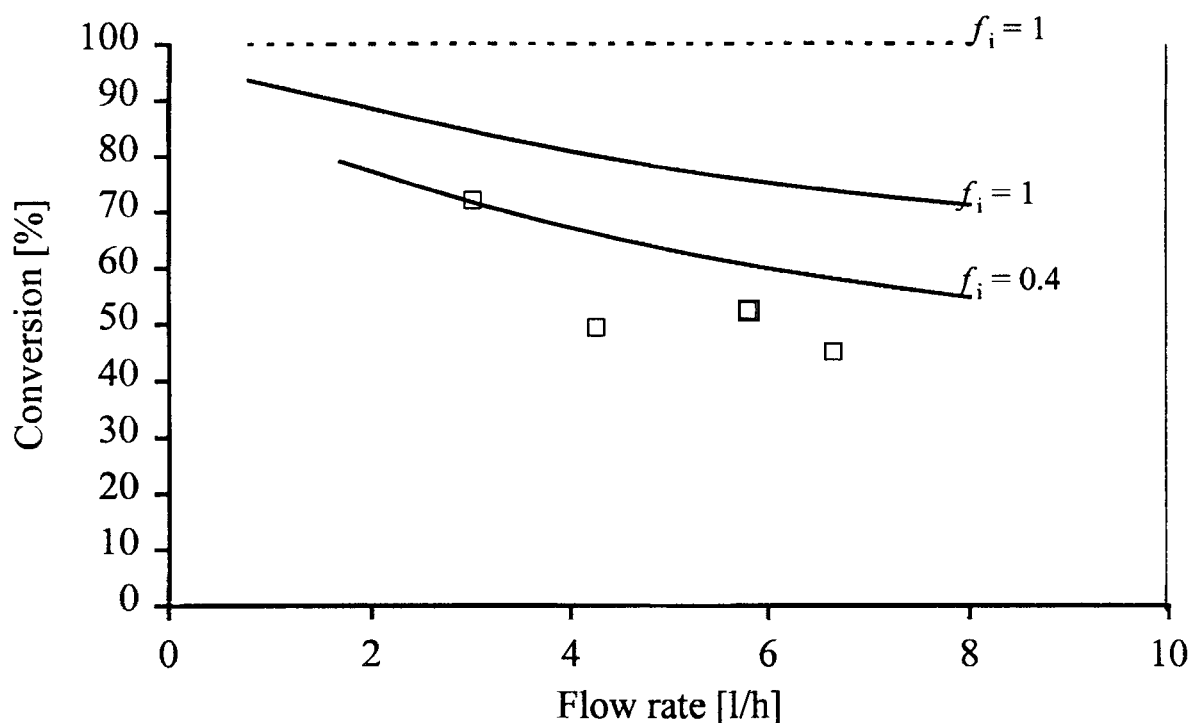


Fig. 3. Polymerization of MMA within Buss-Kneader. Calculated and measured conversions as a function of flow rate. Temperature settings of screw and barrel: 125°C. Experimental (□), calculated without gel effect (—) and calculated including gel effect (- - -). Screw rotation speed is increased proportionally to flow rate from 100 rpm to 220 rpm.

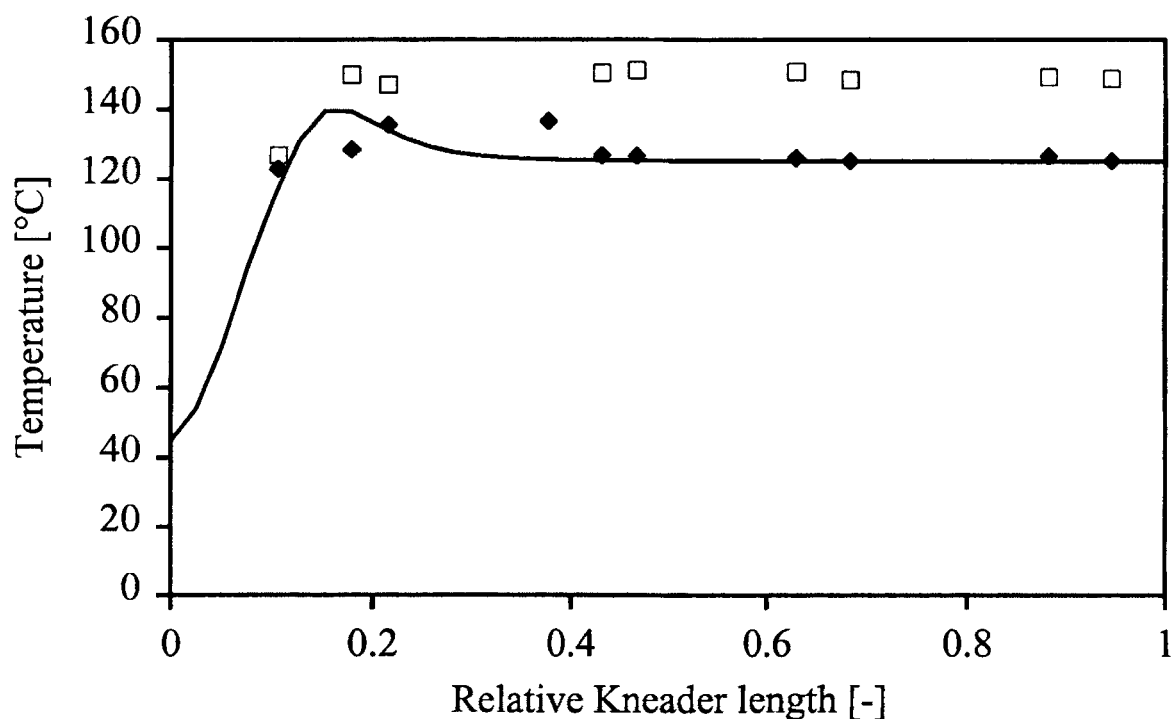


Fig. 4. Measured and calculated axial temperature profiles. Temperature settings of screw and barrel: 125°C. Flow rate is 1.8 l/h. Experimental MMA:nBA:HEMA = 70:15:15 wt%.  $N = 60$  rpm (◆) and  $N = 285$  rpm (□). Calculated without gel effect,  $f_i = 1$ , MMA:nBA:HEMA = 66:15:19 wt% (—).

peroxy-2-ethylhexanoate (Luperox 26R-M-50, Elf Atochem) was added to ensure peroxide activity at high temperatures. Performed calculations are based on 3 wt% tert-amyl peroxy-2-ethylhexanoate.

### Polymerization Kinetics

The polymerization kinetics of the ter-polymerization of MMA, nBA and HEMA have been studied by Maeder (14). The initial monomer ratio of MMA:nBA:HEMA = 66:15:19 wt% used by Maeder is comparable with the ratio of 70:15:15 wt% used in this work. An overall polymerization rate constant defined similar to the rate constant for the homo-polymerization of MMA has been measured. The kinetic constants as measured by Maeder (13) by means of DSC are summarized in Table 3. Maeder observed in his experiments a gel effect and described the termination rate constant with Eq 1.

### Pressure Control and Process Stability

Because of the low viscosity of the polymer, a die diameter smaller than the one used for the homo-polymerization of MMA was necessary to maintain the pressure within the Kneader. An adjustable die with a maximum diameter of 0.5 cm was used. The pressure could be measured at the inlet, halfway and within the die of the Kneader. To avoid evaporation of MMA, a pressure between 7 and 10 bars was maintained throughout the reactor by adjusting the die resistance. Pressures measured halfway in the Kneader and at the inlet were of the same order of magnitude. Pressures measured within the die were about 3 bars. Apparently, the pressure is already reduced at the entrance of the die. Stable processing required a continuous adjustment of the die resistance to keep pressures constant.

### Results

Axial temperature profiles and conversions are calculated using the polymerization kinetics as given in Table 3. Again, good agreement is obtained between calculated and experimentally (MMA:HEMA:nBA =

70:15:15) obtained temperature profiles and conversions if the occurrence of a gel effect is neglected.

At increasing screw speeds ( $N = 285$  rpm), viscous dissipation becomes significant and calculations deviate from measured values (Fig. 4). Viscous dissipation is not included in the model. Figure 5 shows that the overall conversion decreases when the amount of MMA decreases. This is in agreement with the kinetic work of Maeder (13), who concluded that the addition of nBA in this ter-polymerization results in a decrease of the overall polymerization rate.

The molecular weight as measured by means of GPC, calibrated with MMA standards was in the following range:  $\bar{M}_n = 3 - 5$  kg/mole;  $\bar{M}_w = 20 - 35$  kg/mole.  $\bar{M}_n$  and  $\bar{M}_w$  decreased with increasing throughput.

### Insoluble Products

The ter-polymers produced contain insoluble products, especially those with a high HEMA content. Therefore no application tests were performed with the samples produced. The formation of insoluble products with polymerization reactions involving HEMA is not unknown. The insoluble products are probably crosslinked fractions. This crosslinking was observed during the experiments described in this work, where tert-butyl peroxy-2-ethylhexanoate (Luperox 26R) was used as peroxide, as well as by Maeder (13), who used benzoyl peroxide as initiator. The radicals produced by these peroxides have a large bond dissociation energy and are thus capable of inducing crosslinking by hydrogen abstraction.

### CONCLUSIONS

In correspondence with the results described in part I of this paper, the polymerization rate observed during reactive extrusion is lower than the polymerization rate measured in a DSC apparatus. There is a strong indication that the gel effect does not occur in a mixing device like an extruder. It is proposed that molecular diffusion limitation of the termination reaction is eliminated, even at high conversions, as a result of strong micro mixing.

Table 3. Kinetic Parameters Ter-Polymerization of MMA:HEMA:BA=66:19:15 wt%.

Kinetic constant	Value	Unit	Reference
$k_d$ (Luperox 26R-M-50)	$3.83 \cdot 10^{14} \cdot e^{-\frac{129652}{R \cdot T}}$	$s^{-1}$	Elf Atochem
$k_d$ (Luperox 575)	$1.07 \cdot 10^{17} \cdot e^{-\frac{145000}{R \cdot T}}$	$s^{-1}$	Elf Atochem
X (Luperox 26R-M-50 and 575)	2	—	
$k_{t,0}$	$98000 \cdot e^{-\frac{3000}{R \cdot T}}$	$m^3 \text{ mol}^{-1} s^{-1}$	MMA (6)
$k_{t,c}/k_{t,d}$	$\sim 0$ ( $T > 70^\circ\text{C}$ )	—	(6)
$k_p$	$6.0 \cdot 10^5 \cdot e^{-\frac{42200}{R \cdot T}}$	$m^3 \text{ mol}^{-1} s^{-1}$	(14)
$f_i$	1	—	
$\Delta H_p$	60000	$J \text{ mol}^{-1}$	(14)

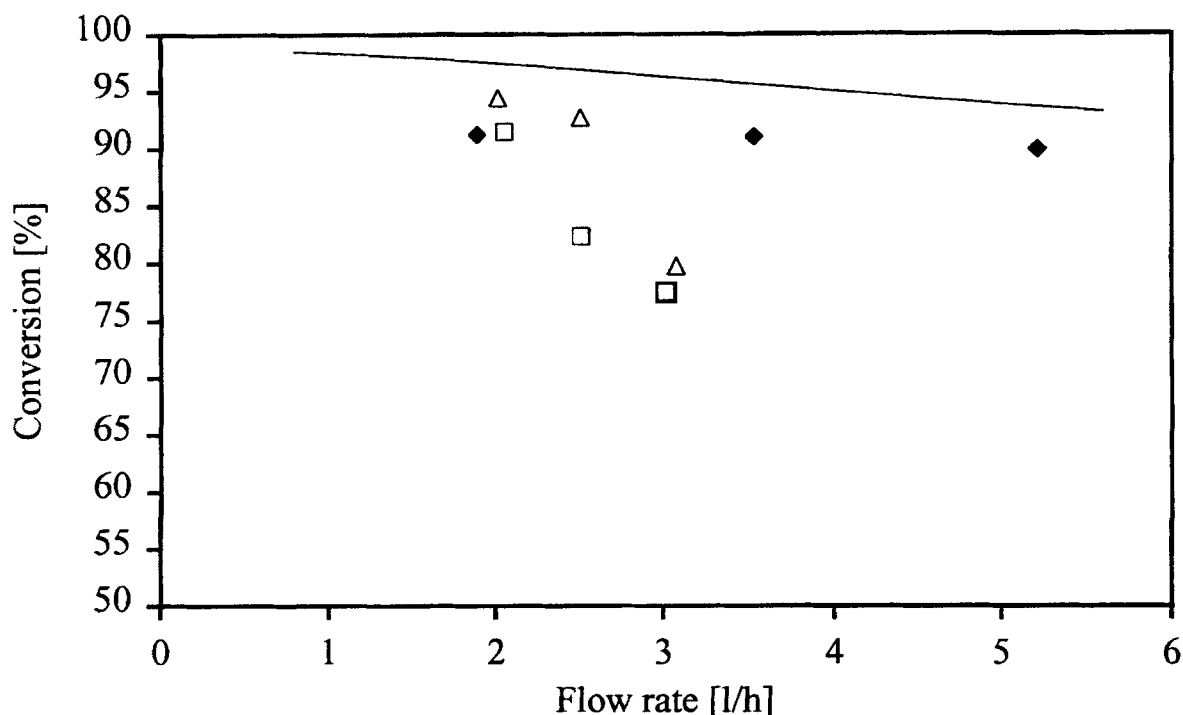


Fig. 5. Measured and calculated conversions as a function of flow rate. Temperature settings of screw and barrel: 125°C. Experimental MMA:nBA:HEMA = 70:15:15 wt%,  $N = 60 - 285$  rpm ( $\sim Q_1$ ) ( $\blacklozenge$ ); MMA:nBA:HEMA = 35:30:35 wt%,  $N = 60$  rpm ( $\square$ ); MMA:nBA:HEMA = 45:20:35 wt%,  $N = 60$  rpm ( $\triangle$ ). Calculated without gel effect,  $f_i = 1$ , MMA:nBA:HEMA = 66:15:19 wt% (—).

The dependency of the die pressure on the degree of fill within an extruder or the Buss-Kneader gives rise to instabilities during reactive extrusion. It is expected that the stability of a reactive extrusion process is improved when a gear pump is used as a discharge device.

The ter-polymer produced from HEMA, MMA, and nBA contained insoluble fractions. Radicals produced by the peroxide used were capable of inducing crosslinking by hydrogen abstraction.

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#### NOMENCLATURE

MMA	methyl methacrylate
HEMA	hydroxyethyl methacrylate
n-BA	n-butylacrylate
Luperox 26R-M-50	commercial name for tert-butyl peroxy-2-ethylhexanoate as a 50 w% solution in iso-dodecane (Elf Atochem)

Luperox 575	commercial name for tert-amyl peroxy-2-ethylhexanoate (Elf Atochem)
I	peroxide molecule
R'	radical from decomposed peroxide
M	monomer molecule
$A_0$	pre-exponential factor
$C_{I0}$	initial initiator concentration $\text{mol m}^{-3}$
$C_{I0, \min}$	model parameter $\text{mol m}^{-3}$
$D_n$	number of dead polymer chains of length $n$ -
$D$	Diameter $\text{m, mm}$
$E$	effective heat axial dispersion coefficient $\text{m}^2 \text{s}^{-1}$
$E_A$	activation energy $\text{J}$
$f_i$	peroxide efficiency -
$k_d$	rate constant for peroxide decomposition $\text{s}^{-1}$
$k_p$	rate constant for propagation $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
$k_{t0}, k_t$	rate constant for termination, index 0 in case of initial value $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
$k_{t,c}, k_{t,d}$	rate constant for termination by combination and termination by disproportionation. $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
$\bar{L}$	length of the reactor $\text{m}$
$\bar{M}_n$	number average molecular weight $\text{kg mol}^{-1}$
$\bar{M}_w$	weight average molecular weight $\text{kg mol}^{-1}$
$M$	Monomer content -



$n$	number of monomer units	-
$N$	screw speed	rpm
$P_{vap}$	vapor pressure	Pa
$P_n$	number of living polymer chains with length $n$	-
$Q_v$	volumetric throughput	l/h
$R$	gas constant (8.3144)	J mol <sup>-1</sup> K <sup>-1</sup>
$R$	reaction rate	mol m <sup>-3</sup> s <sup>-3</sup>
$T$	temperature	K, °C
$T_{ref}$	model parameter	°C
$T_{gp}$	glass transition temperature of polymer	°C
$U$	overall heat transfer coefficient	W m <sup>-2</sup> K <sup>-1</sup>
$V$	reactor volume	l
$X$	Conversion	-
$\alpha, \alpha_0, \beta, \beta_0, \gamma$	Model parameters to describe $k_t$ according to Chiu <i>et al.</i> (5)	-
$\Delta H_p$	polymerization enthalpy	J mol <sup>-1</sup>

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